

## Phase diagram of $\text{UGe}_2$ .

*Whether there are quantum phase transitions ?*

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The phase diagram of several itinerant ferromagnets reveals the common feature. The phase transition temperature decreases with pressure increase and reaches zero value at some critical pressure  $P_c$  such that at low enough temperatures one can expect critical behavior specific for quantum phase transition. It is not the case, however. Being the second order at ambient pressure the transition from paramagnetic to ferromagnetic state at high pressures - low temperatures is transformed to the discontinuous jump.

We discuss the magneto-elastic mechanism of development of the first order type instability at the phase transition to the ferromagnet state in strongly anisotropic ferromagnet  $\text{UGe}_2$ . Using the parameters characterizing the properties of  $\text{UGe}_2$  we argue the effectiveness of this mechanism transforming the very weak first order type transition to the really observable one.

## I. INTRODUCTION

The pressure-temperature phase diagrams of several weak ferromagnets exhibit similarity. The transition from the paramagnetic to the ferromagnetic states at ambient pressure occurs by means of the second order phase transition. The phase transition temperature decreases with pressure increase such that it reaches zero value at some critical pressure  $P_c$ . At some pressure interval below  $P_c$  the ordered ferromagnetic moment disappears discontinuously. Thus at high pressures and low temperatures the ferromagnetic and paramagnetic states are divided by the first order type transition whereas at higher temperatures and lower pressures this transition is of the second order. Such type of behavior is typical for MnSi [1-4], itinerant ferromagnet-superconductor UGe<sub>2</sub> [5,6] (see Fig.1), ZrZn<sub>2</sub> [7]. The same behavior has been established in the ferromagnetic compounds Co(Si<sub>1-x</sub>Se<sub>x</sub>)<sub>2</sub> [8] and (Sr<sub>1-x</sub>Ca<sub>x</sub>)RuO<sub>3</sub> [4] where the role of governing parameter plays the concentration of Se and Ca correspondingly. Also, there was demonstrated clear evidence for the first order nature of the ferromagnetic transitions in typical ferromagnets like Ni, Fe and Co [9].

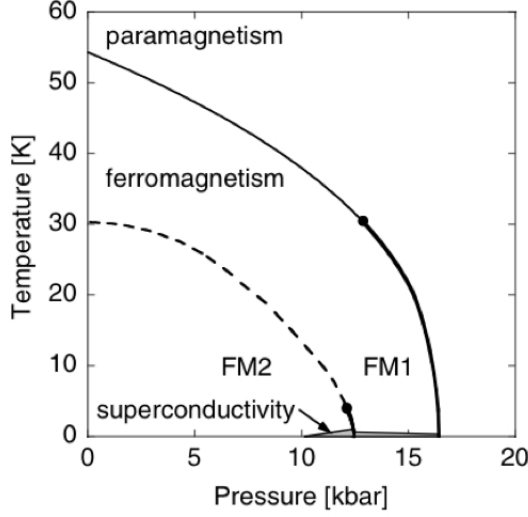


FIG. 1. The schematic phase diagram of UGe<sub>2</sub> Ref. [10]. Thick lines denote first order transitions and fine lines second order transitions. The dashed line is a crossover. Dots mark the positions of critical (tricritical) points.

Here we discuss the magneto-elastic mechanism of development of the first order type instability. Actually the mean field treatment of the magneto-elastic mechanism has been put forward in the paper [11] where it was demonstrated that the change of transition character from the second to the first order takes place at strong enough steepness of the exchange interaction dependence on interatomic distance and large compressibility. It can be considered in frame of the Landau theory of the phase transition. Namely, in neglect the shear deformation the free energy density near the phase transition to the Ising type ferromagnet has the following form

$$F = \alpha_0(T - T_c)M^2 + \beta M^4 + \frac{K}{2}\varepsilon^2 - q\varepsilon M^2. \quad (1)$$

Here,  $M$  is the magnetization density,  $\varepsilon$  is the relative volume change,  $K$  is the bulk modulus. The coefficient  $q$  is related to the Curie temperature pressure dependence as

$$q = \alpha_0 \frac{dT_c}{d\varepsilon} = -\alpha_0 K \frac{dT_c}{dP}. \quad (2)$$

In stress absence  $\frac{\partial F}{\partial \varepsilon} = 0$ , the deformation is determined by square of magnetization  $\varepsilon = \frac{q}{K}M^2$  that yields

$$F = \alpha M^2 + \left( \beta - \frac{q^2}{2K} \right) M^4. \quad (3)$$

Hence, at  $\frac{q^2}{2K} > \beta$  the phase transition changes its character from the second to the first order. This inequality can be rewritten through the measurable parameters as

$$\frac{K\Delta C}{T_c} \left( \frac{dT_c}{dP} \right)^2 > 1, \quad (4)$$

where we used the formula  $\Delta C = \frac{\alpha_0^2}{2\beta}T_c$  for the specific heat jump at phase transition of the second order.

The magneto-elastic interaction also produces another general mechanism for instability of second order phase transition toward to the discontinuous formation of ferromagnetic state from the paramagnetic one. For the first time it was pointed out by O. K. Rice [12] who has demonstrated that at small enough distance from the volume dependent critical temperature  $T_c(V)$ , where the specific heat  $C_{fl}(\tau) \sim \tau^{-\alpha}$ ,  $\tau = \frac{T}{T_c(V)} - 1$ , tends to infinity due to the critical fluctuations, the system bulk modulus  $K = -V \frac{\partial P}{\partial V} = V \frac{\partial^2 FV}{\partial V^2}$ , expressed through the free energy density  $F = F_0 + F_{fl}$ ,  $F_{fl} \sim -T_c \tau^{2-\alpha}$  starts to be negative

$$K = K_0 - A \frac{C_{fl}(\tau)V^2}{T_c} \left( \frac{\partial T_c}{\partial V} \right)^2 = K_0 - AK_0^2 \frac{C_{fl}(\tau)}{T_c} \left( \frac{\partial T_c}{\partial P} \right)^2 \bigg|_{\tau \rightarrow 0} < 0, \quad (5)$$

that contradicts to thermodynamic stability of the system. In reality, before there will be reached the temperature corresponding to  $K = 0$  the system undergoes the first order transition, such that to jump over the instability region directly in the ferromagnetic state with finite magnetization and related to it striction deformation. This transition is similar to the jump over the region with  $\partial P / \partial V > 0$  on the van der Waals isotherm at the liquid-gas transition.

The condition of the first order instability (5) can be written in similar to Eqn.(4) form

$$\frac{K_0 C_{fl}(\tau)}{T_c} \left( \frac{\partial T_c}{\partial P} \right)^2 > 1. \quad (6)$$

However, unlike to Eq. (4) this formula demonstrates that the first order instability is inevitable due to infinite increase of fluctuation specific heat. Thus, if in the system with the fixed volume the phase transition is of the second order with the infinite increase of specific heat then the effect of finite compressibility under assumption that the critical temperature is the volume dependent parameter transforms it into the phase transition of the first order. In reality, the striction interaction can change the shape of the free energy singularity in respect to its form in incompressible case. More elaborate treatment [13] taking into account this effect leads to the following condition of the first order instability  $\frac{1}{T_c} \frac{4\mu K}{3K+4\mu} f''(x) \left( \frac{\partial T_c}{\partial P} \right)^2 > 1$ . Here the function  $f(x)$  determines the fluctuation part of free energy  $F = -T_c f\left(\frac{T-T_c}{T_c}\right)$ ,  $\mu$  is the shear modulus. Usually, the left hand side in Eqn. (6) is quite small and the transition of the first order occurs at temperature  $T^*$  close to the critical temperature where fluctuation specific heat is large enough. It means that the temperature difference  $T^* - T_c$  is smaller than the critical temperature  $T_c$  by many orders. The latent heat at this transition  $q \approx C_{fl}(T^* - T_c)$  proves to be extremely small. So, the first order phase transition is practically indistinguishable from the second order one and called weak first order phase transition or the phase transition of the first order closed to the second order.

According to Eqs (4), (6) the magneto-elastic mechanism effectively leads to the first order transition when the critical temperature is strongly pressure dependent. This is the case in all mentioned above materials. To check the criteria (4), (6) one must calculate the mean field jump and fluctuation part of the specific heat near the Curie temperature for each given material. To be concrete, here, I'll do these calculations for  $\text{UGe}_2$  characterized by strong magnetic anisotropy and by the precipitous drop of the critical temperature at pressure increase near 14-15 kbar [14].

## II. THE SPECIFIC HEAT NEAR THE CURIE TEMPERATURE

$\text{UGe}_2$  is orthorhombic crystal with ferromagnetic order at ambient pressure found below  $T_c = 53 \text{ K}$ . Magnetic measurements reveal a very strong magnetocrystalline anisotropy [15] with  $\mathbf{a}$  being the easy axis. We shall denote it as  $z$  direction. The free energy of strongly anisotropic ferromagnet can be written in terms of one component scalar order parameter corresponding to magnetization density  $M_z(\mathbf{r})$  along  $z$  axis. In that follows we shall omit the order parameter index  $z$ .

$$\mathcal{F} = \int d^3\mathbf{r} \left\{ \alpha M^2 + \beta M^4 + \gamma_{ij} \nabla_i M \nabla_j M - \frac{1}{2} \frac{\partial^2 M(\mathbf{r})}{\partial z^2} \int \frac{M(\mathbf{r}') d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \right\} \quad (7)$$

Here,  $\alpha = \alpha_0(T - T_c)$ , the gradient terms are written taking into account the orthorhombic anisotropy  $\gamma_{ij} = \begin{pmatrix} \gamma_{xx} & 0 & 0 \\ 0 & \gamma_{yy} & 0 \\ 0 & 0 & \gamma_{zz} \end{pmatrix}$ , where the  $x, y, z$  are directions of the spin axes pinned to  $b, c, a$  crystallographic directions correspondingly. The last nonlocal term in Eq. (7) corresponds to magnetostatic energy [16,17]  $-\mathbf{M}\mathbf{H} - H^2/8\pi$ , where

internal magnetic field  $\mathbf{H}$  expressed in terms of magnetization density by means of Maxwell equations  $\text{rot}\mathbf{H} = 0$  and  $\text{div}(\mathbf{H} + 4\pi\mathbf{M}) = 0$ . We shall use the following estimations for the coefficients in the Landau free energy functional

$$\alpha_0 = \frac{1}{m^2 n}, \quad (8)$$

$$\beta = \frac{T_c}{2(m^2 n)^2 n}, \quad (9)$$

$$\gamma_x \approx \gamma_y \approx \gamma_z \approx \frac{T_c a^2}{m^2 n}. \quad (10)$$

Here,  $m = 1.4\mu_B$  is the magnetic moment per uranium atom at zero temperature [18],  $n = a^{-3}$  is the density of uranium atoms, which can be approximately taken equal to inverse cube of the nearest-neighbor uranium atoms separation  $a = 3.85$  Angstrom [19].

The mean field magnetization and the jump of specific heat are

$$M^2 = -\frac{\alpha}{2\beta} = (mn)^2 \frac{T_c - T}{T_c} \quad (11)$$

$$\Delta C = \frac{T_c \alpha_0^2}{2\beta} = n. \quad (12)$$

The experimentally found specific heat jump  $\Delta C_{exp} \approx 10 \frac{J}{molK} \approx 1$  per uranium atom [19] is in remarkable correspondence with Eq.(12).

The effective Hamiltonian of noninteracting field of the order parameter fluctuations is given by

$$H_0 = \sum_{\mathbf{k}} (\alpha + \gamma_{ij} k_i k_j + 2\pi k_z^2 / k^2) M_{\mathbf{k}} M_{-\mathbf{k}}, \quad (13)$$

where  $M_{\mathbf{k}} = \int M(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} d^3\mathbf{r}$ . The corresponding free energy and the specific heat are [20]

$$\mathcal{F}_{fl} = -\frac{T}{2} \sum_{\mathbf{k}} \ln \frac{\pi T}{\alpha + \gamma_{ij} k_i k_j + 2\pi k_z^2 / k^2}, \quad (14)$$

$$C_{fl0} = \frac{T^2 \alpha_0^2}{2(2\pi)^3} \int \frac{dk_x dk_y dk_z}{[\alpha + 2\pi \hat{k}_z^2 + \gamma_{ij} k_i k_j]^2}. \quad (15)$$

Proceeding to spherical coordinates and performing integration over modulus  $k$  we come to

$$C_{fl0} = \frac{T^2 \alpha_0^2}{32\pi^2} \int_0^1 d\zeta \int_0^{2\pi} \frac{d\varphi}{(\alpha + 2\pi \zeta^2)^{1/2} (\gamma_{\perp} + \zeta^2 (\gamma_z - \gamma_{\perp}))^{3/2}}. \quad (16)$$

Here,  $\gamma_{\perp}(\varphi) = \gamma_x \cos^2 \varphi + \gamma_y \sin^2 \varphi$ . At critical temperature  $\alpha = 0$  and the integral diverges. Hence, performing integration over  $\zeta$  with logarithmic accuracy we obtain

$$C_{fl0} = \frac{T_c^2 \alpha_0^2}{32\pi \sqrt{2\pi} \gamma^{3/2}} \ln \frac{\alpha}{2\pi} \approx \frac{n}{32\pi} \sqrt{\frac{T_c}{2\pi m^2 n}} \ln \frac{2\pi m^2 n}{T - T_c}, \quad (17)$$

where

$$\frac{1}{\gamma^{3/2}} = \frac{1}{2\pi} \int_0^{2\pi} \frac{d\varphi}{\gamma_{\perp}^{3/2}(\varphi)}.$$

The used condition  $\alpha \ll 2\pi$  at  $T_c = 10K$  is realized at

$$\frac{T - T_c}{T_c} < \frac{2\pi m^2 n}{T_c} \approx 0.015. \quad (18)$$

In view of roughness of the parameter estimation the region of logarithmic increase of specific heat can be in fact broader.

The calculation taking into account the interaction of fluctuations has been performed by Larkin and Khmel'nitskii [21]. In our notations the expression for the fluctuation specific heat at const pressure obtained in this paper is

$$C_{fl} = \frac{3^{1/3} T_c^2 \alpha_0^2}{16\pi \gamma_{LK}^{2/3} \gamma^{3/2}} \left( \ln \frac{\alpha}{2\pi} \right)^{1/3} \quad (19)$$

Here  $\gamma_{LK} = \frac{3T_c \beta}{\sqrt{32\pi} \gamma^{3/2}}$  is the effective constant of interaction. Using the Eqs. (8)-(10) one can rewrite Eq. (19) as

$$C_{fl} \approx \frac{n}{10} \left( \frac{T_c}{2\pi m^2 n} \right)^{1/6} \left( \ln \frac{2\pi m^2 n}{T - T_c} \right)^{1/3}. \quad (20)$$

So, we see that the order parameter fluctuations give rise the increase of specific heat near the critical point. The power of the logarithm  $(\ln \frac{\alpha}{2\pi})^{1/3}$  is quite slow function slightly exceeding unity, hence in the temperature region given by inequality (18) one may estimate the fluctuation specific heat as

$$C_{fl} > \frac{n}{5}. \quad (21)$$

We see that the fluctuation specific heat is smaller than the mean field jump given by Eqn. (12). Hence to check the first order phase transition instability in UGe<sub>2</sub> one must to proceed with criterium (4).

### III. INSTABILITY OF THE SECOND ORDER PHASE TRANSITION

The Curie temperature in UGe<sub>2</sub> falls monotonically with increasing pressure from 53 K at ambient pressure and drops precipitously above 15 Kbar [14]. The average value of the critical temperature derivative can be estimated as

$$\frac{\partial T_c}{\partial P} \approx \frac{40 \text{ Kelvin}}{14 \text{ kbar}} = 4 \times 10^{-25} \text{ cm}^3 \quad (22)$$

For the bulk modulus we have

$$K = \rho c^2 \approx 10^{11} \text{ erg/cm}^3, \quad (23)$$

where we have substituted typical sound velocity  $c \approx 10^5 \text{ cm/sec}$  and used known [22] density value  $\rho = 10.26 \text{ g/cm}^3$ . Thus, we have for the combination Eq.(4)

$$\frac{Kn}{T_c} \left( \frac{\partial T_c}{\partial P} \right)^2 = 0.2. \quad (24)$$

At  $T \approx 10K$  the pressure derivative of the critical temperature is much higher (and its square is even more higher) than its average value given by Eq. (22). So, we come to conclusion that at critical temperature of the order 10 K the criterium (4) is fulfilled and the phase transition of the second order turns into the first order one.

### IV. CONCLUSION

The magneto-elastic interaction provides development of the first order instability at the phase transition to the ordered state in a ferromagnet. However, actual temperature interval of this instability development is negligibly small and the first order transition looks almost indistinguishable from the second order one. The particular feature of anisotropic ferromagnet UGe<sub>2</sub> is the precipitous drop of the Curie temperature as the function of pressure near 14-15 kbar. Due to this property at about these pressures the second order phase transition (or very weak transition of the first order) to ferromagnet state turns into the real first order type transition.

At low temperatures according to the Nernst law and the Clausius-Clapeyron relation

$$\frac{dT_c}{dP} = \frac{v_1 - v_2}{s_1 - s_2} \Big|_{T \rightarrow 0} \rightarrow \infty \quad (25)$$

the drop of transition temperature with pressure begins to be infinitely fast. It means that weak first order transition has the tendency to be stronger and stronger as temperature decreases. Hence, the effect of magneto-elastic interaction or, more generally, of the order parameter interaction with elastic degrees of freedom at arbitrary type of ordering raises the doubts upon the existence of quantum critical phenomena.

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